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SYNTHESIS AND SINTERING OF CORDIERITE SOL-GEL POWDERS BASED ON DIFFERENT MAGNESIUM SALTS

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The effect of the nature of the magnesium salt on synthesis and sintering of cordierite powders made by the sol-gel method was established. The phase composition of the powder and behavior of the material in sintering are a function of the calcination temperature of the xerogels.

Obtaining a dense finely crystalline, cordierite-based ceramic with optimum properties is a complex problem because of the important rate of collective recrystallization due to the low melting point of cordierite. Cordierite ceramics technology is not considered simple, primarily because of the narrow range of the sintered state. Mass production is based on use of natural raw materials with different additives that widen the range of the sintered state.

It is not possible to obtain a dense cordierite ceramic with the usual technology that includes synthesis from simple or complex oxides or from natural materials (clay, talc, alumina). Highly active powders prepared by chemical methods have recently been used for this purpose.

One of the most promising methods of obtaining highly disperse powders is sol-gel technology [1, 2], primarily due to the simplicity and availability of the reagents and equipment used. The main advantages of this method are the possibility of obtaining ultradisperse powders of complex composition, reducing the synthesis temperature, and the controlled morphology and phase composition of the material.

High-purity cordierite can be synthesized with sol-gel technology, where the components in the liquid state are mixed in the required ratio with an organometallic precursor and a sol-gel system is obtained [3, 4]. We used one version of sol-gel technology, whose principles are proposed in [5, 6], in our study. According to this technology, the components of the synthesized compound in the real or colloidal state, are uniformly distributed and homogeneity of the system persists in the transition to a gel and then on removal of water into a xerogel. However, there are no data on the effect of the gelation conditions on synthesis of cordierite and its subsequent sintering in preparation of powders by the sol-gel method. In particular, the effect of the nature of the initial

compounds on the properties of the sol-gel powders has not been investigated.

The nitrate salt crystal hydrate was used as the aluminum-containing component. Alumina was incorporated in the form of its amorphous modification — “highly dispersed amorphous silica,” and magnesium-containing compounds are represented by the nitrate crystal hydrate, hydroxide, acetate, and carbonate. The components used to synthesize cordierite were uniformly distributed in a solution of an organic polymer, in our case polyvinyl alcohol (PVA), successively initially converted into sol then into gel, and on drying into xerogel. The behavior of the xerogels when heated to the synthesis temperature was monitored by differential thermal analysis. The derivatogram is a complex picture reflecting the processes that take place with each component, they are superimposed on each other, and for this reason shift some other characteristics of the peak, in addition to the effect corresponding to synthesis of the compound.

Since all xerogels contain aluminum nitrate crystal hydrate and PVA, we can distinguish the peaks corresponding to crystal hydrate water by the aluminum nitrate (endothermic effects at low temperatures, under 400°C, related to loss of crystal hydrate water in several stages) and oxidation of the products of decomposition of PVA (exothermic effects in the 440 – 490°C region). The processes that take place with the corresponding magnesium salts are superimposed on these effects.

The endothermic effects in the magnesium nitrate xerogel in the 390 – 440°C temperature region correspond to its decomposition with formation of MgO (Fig. 1). The exothermic effect in the 850°C region is most probably due to the beginning of cordierite formation. This is confirmed by the data from petrographic analysis, where round cordierite crystals and phases preceding cordierite formation, that is, cristobalite in the amount of 60 and 30%, respectively, were

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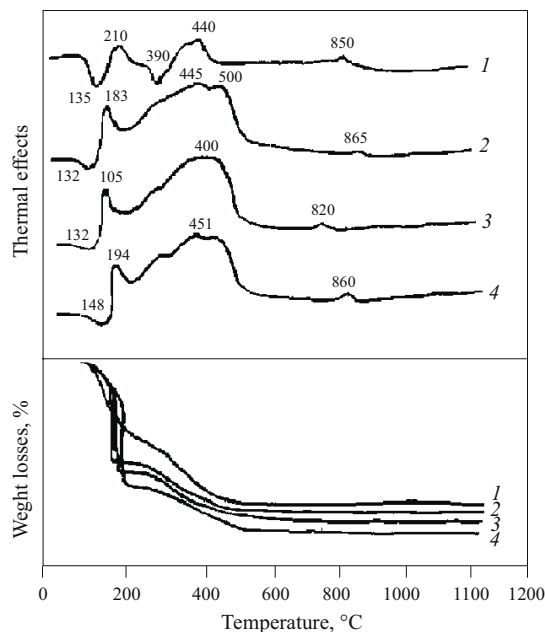


Fig. 1. Differential Thermograms of magnesium salt xerogels: 1, 2, 3, and 4) nitrate, hydroxide, acetate, and carbonate.

found in xerogel powder calcined at 900°C for 2 h. After synthesis at 1000°C, the amount of cordierite (according to data from petrographic analysis) increased to 85%, primarily due to a decrease in the amount of spinel and cristobalite to 10%. In the x-ray pattern, the appearance of cordierite, apparently relatively well crystallized, is identified at 900°C.

In magnesium hydroxide xerogel, cordierite formation takes place relatively actively. At temperatures above 280°C, magnesium hydroxide decomposes with formation of MgO, after losing crystal hydrate water in the 132–260°C range (see Fig. 1). The exothermic effect at 865°C is due to forma-

tion of cordierite. The data from the x-ray phase and petrographic analyses indicates the presence of 45% cordierite. The particles have the same refractive index over the entire volume. When the synthesis temperature was raised from 900 to 1200°C, the amount of cordierite increased (Table 1). The size of the cordierite crystals not only increased to 4 μm, but it began to sinter with formation of intercrystalline porosity (pore size less than 2 μm) due to the high activity of the powder.

The several endothermic effects in the 200–485°C region in the acetate xerogel are due to decomposition of the magnesium salt. The exothermic effect at 820°C is most probably caused by formation of cordierite. Disperse cordierite powder with a particle size of less than 1 μm was obtained during decomposition of the xerogel. The refractive index of the powder particles varies from 1.537 to 1.545. According to the data from x-ray phase and petrographic analyses, synthesis of cordierite takes place through a metastable quartz-like phase (μ-cordierite). When the synthesis temperature is increased from 900 to 1200°C, the amount of cordierite increases. The size of the cordierite crystals not only increase to 3–4 μm, but the α-cordierite content also increases (see Table 1).

Synthesis of cordierite from magnesium carbonate takes place less intensively than in the first case. The $\text{MgCO}_3 \cdot 6\text{H}_2\text{O}$ xerogel decomposes in the 140–240°C range with loss of chemically bound water (see Fig. 1). The endothermic effects in the 250–590°C temperature range indicate decomposition of magnesium carbonate. According to the data from petrographic analysis, decomposition is not complete and even at 900°C, 5–7% undecomposed magnesium carbonate persists. The remainder consists of the metastable phase of μ-cordierite, spinel, and cristobalite. Increasing the temperature to 1200°C causes crystallization of the disperse phase of α-cordierite, and the excess in SiO_2 in the form of cristobalite is 8% (see Table 1).

The most probable explanation of the different activity of magnesium salt anions in synthesis of cordierite consists of the following. During mixing, the components react due to the electrostatic attraction of positively charged magnesium ions and silica particles with the negatively charged surface modified by aluminum cations. This reaction takes place more completely at a pH of the solution close to the pH of the isoelectric point (2.0 ± 0.2). The acetate, carbonate, and hydroxide crystal hydrates create a more basic medium (pH of the solutions of 5.02, 6.64, and 7.59) than the magnesium nitrate crystal hydrates (pH = 2.03) [7].

Adsorption of magnesium cation, which causes the formation of a Si–O–Al–O–Mg bond, takes place due to condensation of hydroxyl groups on the surface of the silica and crystal hydrates of the magnesium salts. In the range of pH = 2–4.5, magnesium cations are adsorbed on the surface of the silica due to formation of hydrogen bonds between surface silanol groups and aluminum nitrates, and at pH = 6–8.5, adsorption of anions of the magnesium salts on

TABLE 1

Powders from magnesium salts	Synthesis temperature, °C	Volume phase content, %				Particle size, μm
		α-cordierite	μ-cordierite	spinel	SiO ₂	
Nitrate	900	25	30	35	10	< 1
Carbonate		5–6	40	40	15	< 1
Acetate		5	80	10	5	< 1
Hydroxide		10	40	35	15	< 1
Nitrate	1000	55	20	15	10	1–1.5
Carbonate		20–25	35–40	30–35	5–10	1–2
Acetate		55	20	15	10	1–2
Hydroxide		50	30	15	5	1–3
Nitrate	1100	65	15	10	10	2
Carbonate		45	35	15	5	1–2
Acetate		70	13	10	7	1–2
Hydroxide		65	15	10	10	1–2
Nitrate	1200	85	10	5	–	3–4
Carbonate		65	25	10	–	1–2
Acetate		75	20	5	–	3–4
Hydroxide		75	10	10	8	3–4

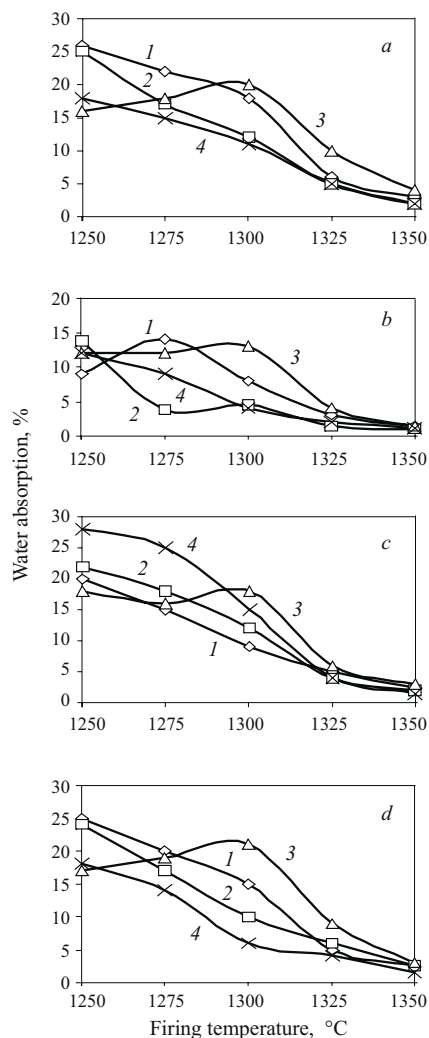


Fig. 2. Water absorption of cordierite ceramic from magnesium salt xerogels: *a*) acetate; *b*) nitrate; *c*) carbonate; *d*) hydroxide; 1, 2, 3, and 4) powder synthesis temperature of 900, 1000, 1100, and 1200°C.

the surface of silica particles with formation of ion pairs, which takes place at higher temperatures, is possible. For this reason, the magnesium compounds are probably in the following order with respect to activity in formation of cordierite: nitrate → acetate → carbonate → hydroxide.

The sinterability of cordierite sol-gel powders was investigated in the 1250–1350°C temperature range with a 25°C step (selected due to the very narrow region of the sintered state of cordierite ceramic, 15–20°C).

Regardless of the temperature of heat treatment of xerogels with a different previous history, the sinterability of the powders has a common character: water absorption decreases with an increase in the temperature (Fig. 2), which corresponds to the generally accepted concepts. The strength of the samples also uniformly increases during compacting (Fig. 3). The decrease in the strength observed for some compositions beginning with the temperature of 1300–

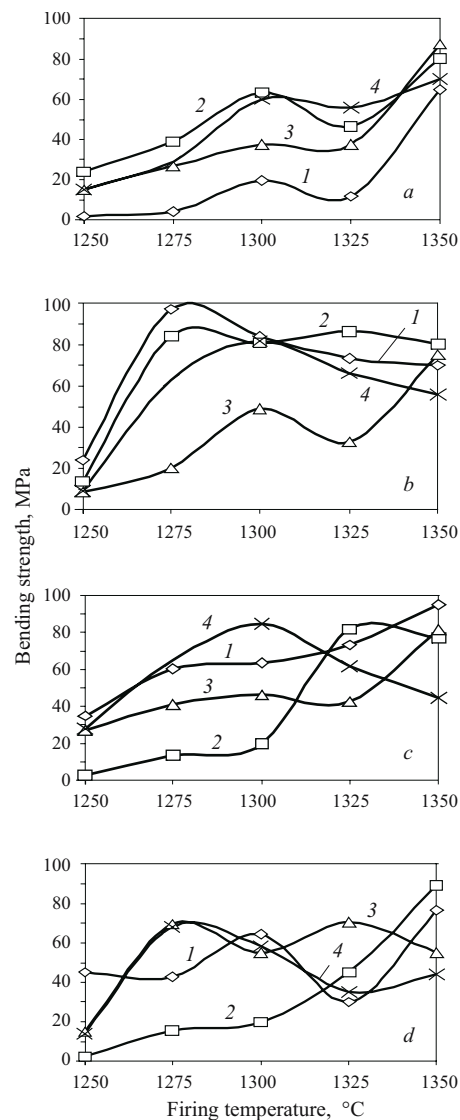


Fig. 3. Strength of cordierite ceramic from magnesium salt xerogels: notation same as in Fig. 2.

1325°C (see Fig. 3) is due to the recrystallization that takes place with an increase in the temperature. In samples of powder synthesized at 900°C and fired at 1250°C, the crystals measure 1–3 μm. The intercrystalline porosity is 2%, and the pore size is less than 1 μm (Table 2). When the temperature is increased to 1300°C, the crystals grow (to 8 μm, and individual crystals reach 12–15 μm in size), and the porosity increases to 10%.

We should also note that beginning at 1350°C, the water absorption of samples of all of the powders increased with an increase in the firing temperature. Since the density of the samples in this case almost does not change, this could be attributed to the increase in open porosity with a simultaneous decrease in the number of closed pores. Beginning at 1350°C, burnout of the ceramic begins, an ordinary event for cordierite which has a narrow sintered-state range [8].

TABLE 2

Ceramic sample		Firing temperature, °C	Size of cordierite crystals, μm	Volume content, %			
based on magnesium salts	powder synthesis temperature, °C			crystalline phases			pores
				α-cordierite	μ-cordierite	spinel	
Nitrate	900	1250	1 – 3	88	7	5	3 – 4
		1300	8 – 12	95	3	2	5 – 6
Carbonate	900	1250	1 – 3	55	25	20	3 – 4
		1300	6 – 8	70	20	10	7 – 8
Acetate	900	1250	1 – 2	75	10	15	2 – 3
		1300	8 – 10	82	8	10	10 – 12
Hydroxide	900	1250	1 – 3	68	17	15	1 – 2
		1300	6 – 15	70	15	15	7 – 8
Nitrate	1000	1250	2 – 4	85	5	10	5 – 6
		1300	8 – 10	95	3	2	1 – 2
Carbonate	1000	1250	2 – 4	60	20	20	3 – 4
		1300	6 – 12	73	15	12	10 – 12
Acetate	1000	1250	2 – 4	78	10	12	3 – 4
		1300	6 – 15	85	8	7	5 – 6
Hydroxide	1000	1250	3 – 4	72	15	13	3 – 4
		1300	8 – 12	80	10	10	5 – 6

The structure of the cordierite samples synthesized at 1000°C and fired at 1350°C is also characterized by inhomogeneity of crystallization (2 – 10 μm crystal size, approximately 7% intercrystalline porosity, glassy phase in the form of agglomerates up to 4 μm in size).

Despite the complexity of sintering cordierite sol-gel powders and the difficulty in obtaining a dense ceramic from them due to the narrow region of the sintered state, the densest ceramic can be obtained by using magnesium nitrate and acetate powders synthesized at 1000°C and magnesium carbonate and hydroxide powders synthesized at 1100°C. These powders already have a sufficient degree of cordierite formation, in contrast to powders calcined at 900°C, and a higher specific surface area in comparison to powders fired at 1200°C.

Cordierite is synthesized at relatively low temperatures. Active, highly disperse powders are obtained, but their temperature of sintering to a dense state is relatively high (approximately 1275°C) and the region of the sintered state is insignificantly expanded in the given case.

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